

HIGHLY ACTIVE W-H₂SO₄/HZSM-5 CATALYST FOR DIRECT CONVERSION OF METHANE INTO AROMATIC

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Abstract

Dehydroaromatization of methane (DHAM) under non oxidative condition was studied over tungsten loaded HZSM-5 catalysts to produce aromatic hydrocarbons. The catalysts were prepared by impregnation method using different conditions: in neutral and acidified solution. The activity of W/HZSM-5 prepared by neutral solution and W-H₂SO₄/HZSM-5 prepared in acidified condition were compared. The results showed that the optimum activity of W-H₂SO₄/HZSM-5 catalyst exceeded that of W/HZSM-5 catalyst. The effect of Si/Al ratio of W- H₂SO₄/HZSM-5 catalyst was also studied. The W- H₂SO₄/HZSM-5 catalyst with Si/Al ratio = 30 was found to be the most promising for the DHAM reaction. The remarkable activity of the catalyst is attributed to the presence of dual effects: suitable content of octahedral polymeric and tetrahedral monomeric tungstate species accompanied by proper amount and strength of acid sites in the catalyst.

Kata kunci: methane; aromatization; W/HZSM-5

Introduction

Methane, the main component of natural gas is an important source of energy. Currently, the main use of natural gas is combustion process for heating purposes. However, the usage of natural gas for liquid fuels and higher hydrocarbon is limited. Direct conversion of methane to more valuable chemicals is still a challenging field in catalysis (Hassan *et al.*, 2006).

Previous studies have been conducted on dehydroaromatization of methane (DHAM). The studies reported that the DHAM reaction could take place in the presence of HZSM-5 catalysts containing transition metal. Most research work has mainly used Mo metal supported HZSM-5-catalyst operated at 973 K. At such low temperature, methane conversion (XCH₄) was low due to thermodynamic limitation (Xiong *et al.*, 2001). To reach a high methane conversion, higher reaction temperature is required. However, Mo-based catalysts used for DHAM suffers inevitably due to serious loss of Mo component by sublimation under such high temperature. Therefore, it is of interest to find the catalyst with high activity and stabil at higher operation temperatures suitable for DHAM reaction.

The previous works reported that the activity and stability of catalyst can be improved by the addition of a second metal component on Mo/HZSM-5 (i.e Ru or Zn on Mo/HZSM-5). Currently, W/HZSM-5 catalyst was also reported to have highly active catalyst for DHAM reaction in the absence of oxygen. Xiong *et al.* (2001) reported that incorporation of Zn (or Mn, La, Zr) into the W/HZSM-5 catalyst could improve the performance of the catalyst for DHAM reaction operating under higher temperatures. The present work studies the DHAM reaction over W supported HZSM-5 catalysts.

The effects of preparation conditions and Si/Al ratios of HZSM-5 are reported.

Material and Methods

Preparation and characterization of catalyst

The 3%W/HZSM-5 catalyst was prepared by the conventional impregnation method. The HZSM-5 zeolite with a SiO₂/Al₂O₃ ratio of 30 was supplied commercially (Zeolyst international Co. Ltd.). After impregnation with an aqueous solution of ammonium meta tungsten ((NH₄)₆W₁₂O₄₀.H₂O), the zeolite was dried at 120 °C for 2 h, and calcined in static air at 500°C for 5 h. Another set of a series of 3% W-H₂SO₄/HZSM-5 catalysts with different Si/Al ratios were prepared by impregnating HZSM-5 with ((NH₄)₆W₁₂O₄₀.H₂O) and H₂SO₄ solution (pH = 2–3). The acidity of the catalysts was measured by means of TPD-ammonia using a Micromeritics TPD/TPR/O analyzer. The nature of W species on the catalysts was determined by means of UV diffuse reflectance spectra. UV DRS spectra were performed on a Perkin-Elmer Lambda-900 spectrometer.

Catalytic testing

Catalytic testing was carried out at atmospheric pressure in a fixed-bed continuous flow system with a quartz reactor of 9 mm internal diameter and 300 mm length. Before reaction, the catalyst was pretreated in a flow of nitrogen at Feed gas containing CH₄ + 10% N₂ was passed through over the catalyst bed at GHSV of 1800 ml/(g.h). Nitrogen was used as an internal standard for calculating the methane conversion and selectivity of the reaction products. The reaction products were analyzed by a Hewlett-Packard 5890 on-line GC

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equipped with TCD using Porapak Q, molecular sieve 5A, UCW 982, and DC 200 columns.

Results and Discussion

The result of catalysts activity can be seen in Table 1. The catalysts were prepared by impregnating HZSM-5 using different solution of ammonium metatungstate, 3% W/HZSM-5 prepared in neutral solution and 3%W- H₂SO₄/HZSM-5 acidified solution catalysts prepared in acidified solution. The result shows that 3%W-H₂SO₄/HZSM-5 gives higher methane conversion (9.59%) than W/HZSM-5 (8.40%). The results show that 3%W-H₂SO₄/HZSM-5 displays the highest aromatics selectivity (99.5%). It appears that the acidified catalyst give benefit on the activity of catalyst for increasing methane conversion and selectivity to aromatic.

Table 1. Catalytic activity of 3% W/HZSM-5 and 3% W-H₂SO₄/HZSM-5 prepared by neutral and acidified solution, respectively for dehydroaromatization of methane at 973 K, GHSV = 1800 ml/(g.h) , Feed Gas = CH₄ + 10% N₂, 1 atm at 973 K.

Catalyst	Methane conversion (%)	Aromatic selectivity (%)
3%W/HZSM-5 (Si/Al=30)	8.40	98.23
3%W-H ₂ SO ₄ /HZSM-5 (Si/Al=30)	9.59	99.35

The effect of Si/Al ratios on the catalytic performances of W- H₂SO₄/HZSM-5 catalyst for methane dehydrogenation and aromatization at 800 °C, 1 atm and GHSV of 1800 ml/(g.h) catalysts are shown in Figure 1. Feed gas contains a mixture of CH₄ 90% + N₂ 10%. As illustrated in Figures 1A and 1B, the conversion of methane, the selectivity to benzene decreased with increasing Si/Al ratio of HZSM-5. The selectivity to aromatic over the W-H₂SO₄/HZSM-5 (Si/Al =50) catalyst was close to that over the Si/Al =80 catalyst. A methane conversion over 3%wt W- H₂SO₄/HZSM-5 catalyst with Si/Al = 30 approaches a maximum value of 22.08%, and further decreases with time. A maximum aromatic selectivity of 97.49% was achieved over the 3% W- H₂SO₄/HZSM-5 (Si/Al ratio = 30) catalyst. On the other hand, the C₂ selectivity of 3% W-H₂SO₄/HZSM-5 catalyst with various Si/Al ratios increase with an increase in the time on stream, as seen in Figure 1 (C). A gradual but significant increment in the on-stream C₂ selectivity from 2.69% to 12.19% was observed over the 3% W- H₂SO₄/HZSM-5 catalyst with Si/Al = 30.

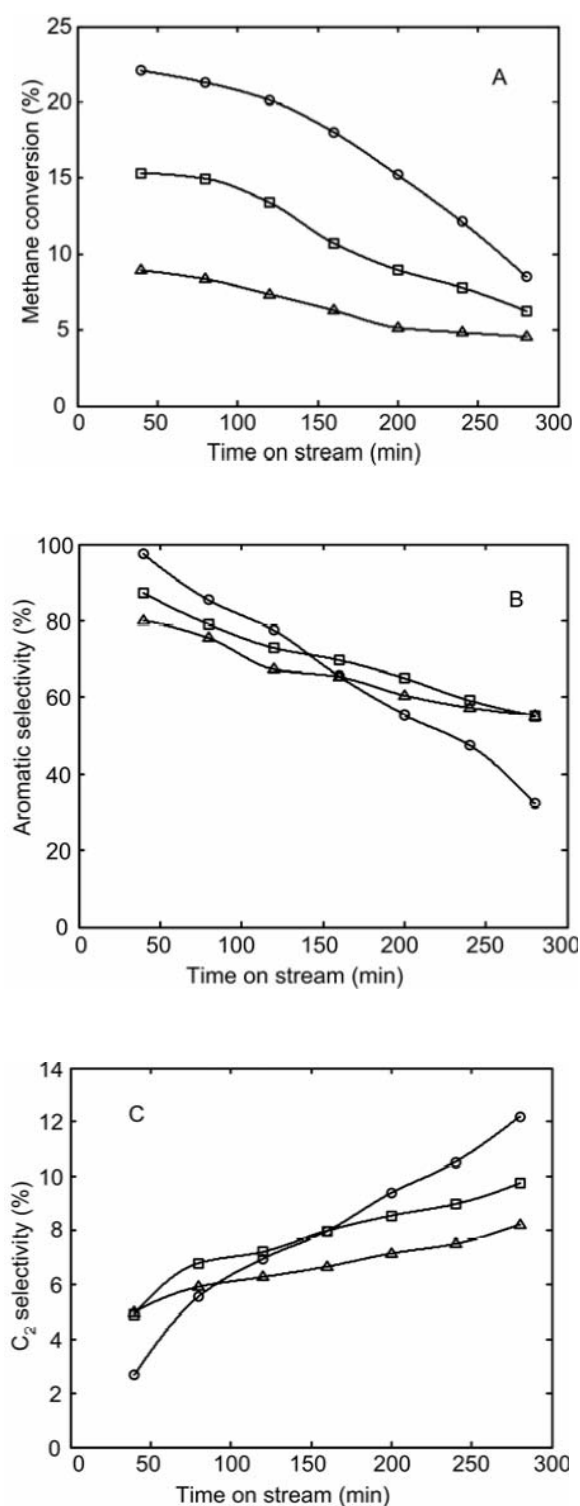


Figure. 1. Catalytic performances for methane dehydrogenation and aromatization at 1073 K, GHSV = 1800 ml/(g.h) and a on the 3%W- H₂SO₄/HZSM-5 (Si/Al=30) (O), (Si/Al=50) (□) and (Si/Al=80) (Δ) catalysts (A) for methane conversion; (B) for benzene selectivity; (C) for C₂ selectivity.

Further investigation was carried out to study the effect of GHSV on the catalytic activity of W-H₂SO₄/HZSM-5 with different Si/Al ratios. During

the studies, the GHSV was conducted in the range of 1800 – 9000 ml/(g.h). The methane conversion, the selectivity to aromatic and C₂-hydrocarbons, are shown in Figures 2A, 2B, 2C, respectively. Figure 2A showed that the methane conversion decreased with the increasing of GHSV. Figure 2A and 2B indicating that large GHSV is unfavorable to methane conversion and formation of aromatics product. Whereas, C₂ hydrocarbons selectivity increased obviously with increasing in GHSV as shown in Figure 2C.

In order to understand the correlation between activity of the catalysts and the catalysts acidity, characterization of the catalysts were conducted. The amount and the strength of the catalysts acidity were determined by means of TPD ammonia. The total number of acid sites and the number of weak and strong acidity measured by NH₃-TPD are listed in Table 2.

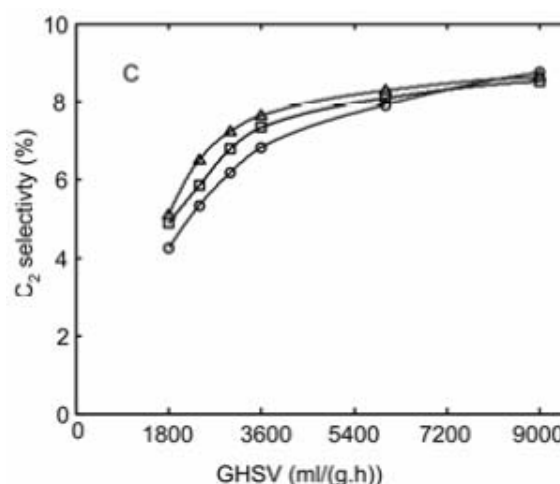
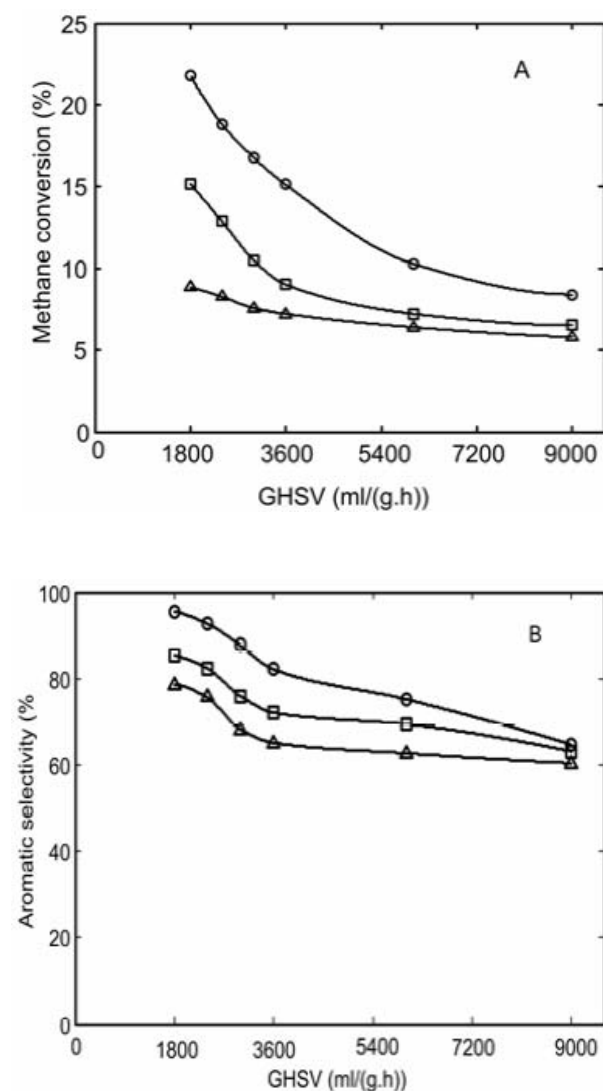


Figure 2. Effect of Si/Al ratio of HZSM-5 on the methane conversion and product selectivities over 3 wt.% W- H₂SO₄/HZSM-5 catalysts for dehydroaromatization of methane at 1073 K, GHSV = 1800 ml/(g.h). Feed Gas = CH₄ + 10% N₂, 1 atm. Catalysts: (O) W-H₂SO₄/HZSM-5 (Si/Al = 30); (□) W-H₂SO₄/HZSM-5 (Si/Al = 50); (Δ) W-H₂SO₄/HZSM-5 (Si/Al = 80).

The amount of desorbed ammonia and desorption temperature are directly associated to the amount and strength of catalyst acidity, respectively. The NH₃-TPD of HZSM-5 has both weak and strong acid sites. The existence of the strong and weak acidity has been reported for the acid characterization of HZSM-5 by the NH₃-TPD method (Shu *et al.*, 1997). The W/HZSM-5 and W- H₂SO₄/HZSM-5 catalysts contain two types of acidic sites: strong acidity (H) and weak acidity (L). The appearance of both the L and H acidity for the transition metal loaded on HZSM-5 samples has been previously reported (Tan *et al.*, 2002). The total number of acid sites and amount of strong acid decreased with the loading of tungsten to HZSM-5 as shown in Table 2. The amount of acid sites on W-H₂SO₄/HZSM-5 catalysts prepared with the addition of H₂SO₄ in the impregnation solution is reduced compared to the W/HZSM-5 catalyst prepared with neutral solution in the impregnation method. The result in Table 2 shows that the amount of acid sites on W-H₂SO₄/HZSM-5 decreases as the ratio Si/Al in of HZSM-5 increases. The data indicates that the amounts of strong acid sites depend substantially on Si/Al ratios of HZSM-5 used. Based on the activity results, it is found that 3% W- H₂SO₄/HZSM-5 (Si/Al = 30) exhibits a maximum aromatics selectivity which decreases significantly with time as presented in Figure 1(B). Moreover, the effect of GHSV on the activity of 3%W-H₂SO₄/HZSM-5 catalysts with different Si/Al ratios indicates that the maximum activity appears on the catalyst with Si/Al = 30 as shown in Figures 2(A)

Table 2. The acidic sites of the samples: parent HZSM-5 ;3% W/HZSM-5 and 3% W-H₂SO₄/ HZSM-5 with various Si/Al ratios of HZSM-5 from NH₃-TPD. Peak L (weak acidity) at T ~ 523 K ; Peak H (strong acidity) at T ~ 743 K.

Catalyst	Amount of NH ₃ -desorbed (mmol/g.cat)		Total number of acid sites (mmol/g.cat)
	Peak L	Peak H	
HZSM-5	0.844	0.407	1.251
W/HZSM-5 (Si/Al=30)	0.698	0.363	1.062
W-H ₂ SO ₄ /HZSM-5 (Si/Al=30)	0.614	0.240	0.854
W-H ₂ SO ₄ /HZSM-5 (Si/Al=50)	0.561	0.127	0.687
W-H ₂ SO ₄ /HZSM-5 (Si/Al=80)	0.356	0.111	0.467

and 2(B) for methane conversion and aromatics selectivity, respectively. This fact might be due to the presence of extensive amount of strong Brönsted acid sites in the 3% W-H₂SO₄/HZSM-5 (Si/Al = 30) catalyst. From the TPD-NH₃ results, the highest amount of strong acidity is presented over the 3% W-H₂SO₄/HZSM-5 (Si/Al = 30) catalyst. It has been reported that the strong Brönsted acid sites on the catalyst were responsible for the formation of aromatics, however, an excess of the Brönsted acid sites led to severe coke formation (Liu and Xu, 1999). The deactivation of the catalyst yielded the decrease in the selectivity for aromatics, whereas the C₂ selectivity increased markedly as evident from the results illustrated in Figures 1B and 1C, respectively. This result suggests that the coke formation in the catalyst could reduce the amount of Brönsted acid sites and the catalyst pore size which may lead to the suppression of C₂-hydrocarbons oligomerization to form benzene. In order to comprehend the relationships between the dehydroaromatization activity of methane and the nature of W species, the UV-DRS characterization was conducted. The different behavior exhibited by the W/HZSM-5 and W-H₂SO₄/HZSM-5 (Si/Al = 30) might be due to the alteration in the nature of W species by the different preparation conditions employed in the impregnation of W on the HZSM-5. The UV-DRS characterization was carried out to provide the evidence for the existence of different kinds of tungsten species and the result is shown in Figure 3. The UV-DRS spectrum of W-H₂SO₄/HZSM-5 consists of two major bands at around 220 nm and 310 nm which correspond to the presence of tetrahedral monomeric and octahedral polymeric tungstate species, respectively. Meanwhile, a major band at 220 nm and a shoulder at 275 nm appear on W/HZSM-5 indicating that tetrahedral monomeric tungstate species are predominant while octahedral polymeric tungstate species exist in a minor extent. The catalyst prepared with the addition of H₂SO₄ in the impregnation solution exhibited considerable amount of polymeric tungstate present in the W-supported catalyst whereas the catalyst prepared in neutral solution had polymeric tungstate in minor amount. The addition of

H₂SO₄ in the impregnation solution can enhance the formation of polytungstate in the precursor which is in accordance with the work reported by several authors (Zhang *et al.*, 1998). The higher activity obtained over the W-H₂SO₄/HZSM-5 catalyst than the W/HZSM-5 catalyst can be attributed to the existence of a considerable amount of octahedral polymeric tungstate species which promote the activity of the W-H₂SO₄/HZSM-5 catalyst.

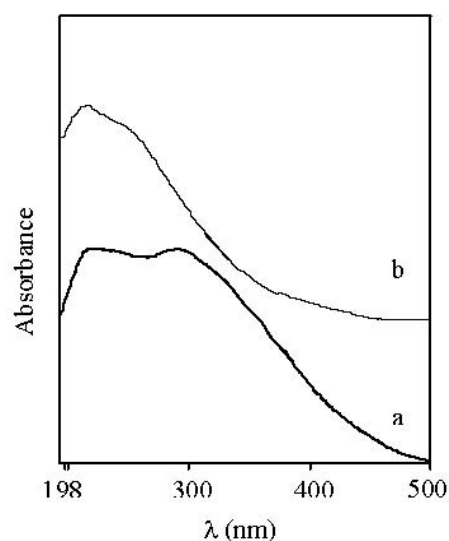


Figure 3. UV-DRS of (a) 3 % W- H₂SO₄/HZSM-5 (Si/Al=30) and (b) 3 % W/HZSM-5 (Si/Al=30)

This result of the activity testing shows that the maximum activity on the W-H₂SO₄/HZSM-5 (Si/Al = 30) catalysts is not only affected by the catalyst acidity, but also by the existence of octahedral polymeric W species. Moreover, the result concludes that the optimum activity of W-based catalysts for DHAM depend on the balanced amount between the two active sites in the catalyst, i.e. acidity and existence of octahedral polymeric and tetrahedral monomeric tungstate species.

Conclusion

Dehydroaromazation of methane (DHAM) was studied over 3 wt% W/HZSM-5 and W-H₂SO₄/HZSM-5 catalysts with different Si/Al ratios of HZSM-5 with GHSV between 1800-9000 ml/(g.h). The W-H₂SO₄/HZSM-5 catalyst exhibited the maximum catalytic activity which is higher than that over W/HZSM-5 prepared by impregnating the HZSM-5 precursor with a neutral solution of ammonium tungstate. The W-H₂SO₄/HZSM 5 catalyst with Si/Al = 30 showed an optimum methane conversion and aromatic selectivity. The relationship between the activity and the characteristics of the catalyst indicated that suitable content of octahedral polymeric and tetrahedral monomeric tungstate species accompanied by proper amount and strength of acid sites in the catalyst contributed to the highest catalytic performance for DHAM.

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